

# ESCA STUDIES OF

VANADIUM OXIDE, SUPPORTED RHODIUM AND UNSUPPORTED RUTHENIUM

# HETEREGENOUS CATALYSTS

by

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Department of Chemical Technology

Lund Institute of Technology

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Sweden

DISSERTATION

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Thesis for the degree of Doctor of Technology.

To be presented, with the permission of the Faculty of Technology  
of the University of Lund, for public criticism in Lecture-hall C  
at the Chemical Center, Lund, on May 21, 1982 at 10.15 a.m.



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| Organization<br>LUND UNIVERSITY<br>Department of Chemical Technology<br>Chemical Center<br>Lund Institute of Technology<br>P.O.Box 740, S-220 07 LUND, Sweden                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  | Document name<br>DOCTORAL DISSERTATION                                                                                     |                     |
| Author(s)<br>S. Lars T. Andersson                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  | Date of issue<br>May 1982                                                                                                  |                     |
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| Sponsoring organization                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | Title and subtitle<br>ESCA Studies of Vanadium Oxide, Supported Rhodium and Unsupported Ruthenium Heterogeneous Catalysts. |                     |
| Abstract<br><p>X-ray photoelectron spectroscopy (XPS, ESCA) has been applied in investigating some heterogeneous catalysts. Both the quantitative and qualitative features have been utilised. The catalysts studied are: <math>V_2O_5/TiO_2</math> and <math>V_2O_5/SnO_2</math> catalysts for the selective oxidation of alkylpyridines, supported Rh catalysts for carbonylation of methanol and unsupported Ru catalysts for liquid phase hydrogenation of benzene to cyclohexene.</p> <p>The initial state of both types of <math>V_2O_5</math> catalysts was studied. The state of used catalysts and the influence of some reaction parameters were also investigated.</p> <p>The initial state of Rh - originating from <math>RhCl_3</math>, <math>(Rh(NH_3)_5Cl)Cl_2</math> and <math>Rh_6(CO)_{16}</math> - supported on zeolite 13X, mordenite, MgO, <math>SnO_2</math>, <math>SiO_2</math> and <math>Al_2O_3</math>, but also the effect of various heat treatments and adsorption of CO and <math>CH_3I</math> were studied.</p> <p>The precursor to the Ru catalysts, the activated used catalysts and the effects on the activated catalysts of the addition of iron and titanium salts at the preparation were also studied.</p> |  |                                                                                                                            |                     |
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| Classification system and/or index terms (if any)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |                                                                                                                            |                     |
| Supplementary bibliographical information                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |                                                                                                                            | Language<br>English |
| ISSN and key title                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                                                                                                                            | ISBN                |
| Recipient's notes                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  | Number of pages<br>168                                                                                                     |                     |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | Price                                                                                                                      |                     |
| Security classification                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  | Price                                                                                                                      |                     |
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ESCA STUDIES OF VANADIUM OXIDE, SUPPORTED RHODIUM  
AND UNSUPPORTED RUTHENIUM HETEROGENEOUS CATALYSTS.

The thesis consists of this summary and the following papers concerning three areas of catalysis.

A. VANADIUM OXIDE CATALYSTS FOR THE SELECTIVE OXIDATION  
OF ALKYLPIRIDINES.

1. ESCA Investigation of  $V_2O_5$  +  $TiO_2$  Catalysts for the Vapour Phase Oxidation of Alkylpyridines.

*S. Lars T. Andersson*

*J. Chem. Soc., Farad. Trans. I, 75(1979)1356-1370.*

2. Activity Measurements and ESCA Investigations of a  $V_2O_5/SnO_2$  Catalyst for the Vapour-Phase Oxidation of Alkylpyridines.

*S. Lars T. Andersson and S. Järås*

*J. Catal., 64 (1980) 51-67.*

B. SUPPORTED RHODIUM CATALYSTS FOR METHANOL CARBONYLATION.

3. Infrared and ESCA Studies of a Heterogenized Rhodium Carbonylation Catalyst.

*S. Lars T. Andersson and Michael S. Scurrell*

*J. Catal., 59(1979) 340-356.*

4. Studies by ESCA of Supported Rhodium Catalysts Related to Activity for Methanol Carbonylation.

*S. Lars T. Andersson and Michael S. Scurrell*

*J. Catal., 71(1981) 233-243.*

5. An XPS Study of  $\text{Rh}_6(\text{CO})_{16}-\text{Al}_2\text{O}_3$

S. Lars T. Andersson, Kenneth L. Watters and

Russell F. Howe

*J. Catal.*, 69(1981) 212-215.

C. UNSUPPORTED RUTHENIUM CATALYSTS FOR LIQUID PHASE  
HYDROGENATION OF BENZENE TO CYCLOHEXENE.

6. Hydrogenation of Benzene to Cyclohexene on a Ruthenium  
Catalyst: Physical and Chemical Characterisation of the  
Catalyst and its Precursor.

C. U. Ingemar Odenbrand and S. Lars T. Andersson

*J. Chem. Tech. Biotechnol.*, 32(1982) 365-375

7. Hydrogenation of Benzene to Cyclohexene on an Unsupported  
Ruthenium Catalyst: Physical and Chemical Characterisation  
of Iron Poisoned Catalysts in Relation to their Catalytic  
Performance.

C. U. Ingemar Odenbrand and S. Lars T. Andersson

*J. Chem. Tech. Biotechnol.*, Accepted for publication.

8. Hydrogenation of Benzene to Cyclohexene on an Unsupported  
Ruthenium Catalyst: An ESCA Study of Titanium Poisoned  
Catalysts.

C. U. Ingemar Odenbrand and S. Lars T. Andersson

*J. Chem. Tech. Biotechnol.*, Submitted for publication.

## Introduction

ESCA (Electron Spectroscopy for Chemical Analysis) or XPS (X-ray Photoelectron Spectroscopy) - described in several books (1-8) and periodic volumes (9) - has during the last decade proved to be a powerful tool for research in heterogeneous catalysis (10-16). It is based on the analysis of the kinetic energy of Auger and photo-electrons emitted from a substance on X-ray irradiation. The emitted photoelectrons receive a kinetic energy according to the photoelectric law:

$$E_K = h\nu + E_i - E_f - \phi$$

where  $E_K$  is the kinetic energy of the photoelectron as measured in the spectrometer,  $h\nu$  is the photon energy,  $E_i$  is the total energy of the system before ionization,  $E_f$  is the final state energy after ionization and  $\phi$  is a correction term which depends on the reference level, spectrometer adjustment and sample charging. Both core and valence electron spectra are obtained.

The, commonly denoted, electron binding energy (BE) is the difference between the final state and initial state energies and is thus determined from the measurement of the photoelectron kinetic energy  $E_K$ . The binding energy of core levels usually differs when an element is present in different chemical environments. The usual interpretation of this "chemical shift" is done in terms of initial state properties, i.e. a true chemical shift is assumed reflecting a change in the ground state of the system. However, final state effects are also of importance and a part of the apparent chemical shift can be due to changes in the relaxation of the electron orbitals. Other final state effects such as multiplet splittings and multi-electron excitations may give interesting chemical information.

Except that both an elemental identification and an elucidation about the chemical state of the elements present may be obtained from ESCA spectra, derivation of quantitative information is also feasible. The intensity of a specific core line from one element is simplifyingly expressed as depending on the number

of atoms of the element in the sampling volume, the probability of photoemission, the electron inelastic mean free path and a complex instrumental function. By performing a set of calibrations and comparing intensities of core lines from different elements in the same substrate the elemental concentrations will be given by;

$$C_x = 100 \times \frac{A_x \cdot R_x}{S_x} / \sum \frac{A_x \cdot R_x}{S_x}$$

where  $C_x$  is the concentration of the element X in atom percent,  $A_x$  the intensity taken as the area of the core line from element X,  $R_x$  the count rate setting and  $S_x$  the sensitivity factor for the specific core line from element X. The sum is performed over all elements included in the calculation. Besides performing a calibration, the sensitivity factors can be calculated at various levels of sophistication. The last but no less important feature of ESCA spectroscopy that makes it suitable for studies in heterogeneous catalysis is the extreme surface sensitivity. This is due to the very low electron inelastic mean free path in solids, which for the energy interval of interest is roughly proportional to the square root of the kinetic energy and ranges from approximately 5-25 Å. This implies that the uppermost atomic layer contributes significantly to the spectra. In fact a fraction of a monolayer, as low as 0.01, can be detected on a sample area of  $0.5 \text{ cm}^2$ . Consequently, applications in catalysis will reveal information about the chemical composition in the surface of the catalyst as well as direct information from adsorbed species.

In this work ESCA spectroscopy has been applied in studies in three areas of heterogeneous catalysis; selective oxidation, carbonylation and selective hydrogenation with emphasis on elucidation of the chemistry of the catalytic processes.

With the exception of a few noble metals, transition metal oxides are used as catalysts for partial oxidation in industrial processes.<sup>17,18</sup> Vanadium oxide based catalysts are amongst the most commonly used ones, and have been studied to a great extent. One of the reactions of more recent interest is the selective oxidation of alkylpyridines to pyridinemono-carboxylic acids.<sup>19,20</sup>

Vanadium oxides have in this work been studied in correlation to the catalytic activity and selectivity in these reactions in order to shed some light on the chemistry of these catalytic processes.

Synthesis gas is gaining an increased interest for various direct or indirect synthetic routes to important bulk and fine chemicals<sup>21</sup> and the abundance of potential reactions are great.<sup>22</sup> For example, acids may be prepared from alcohols by a simple insertion of carbon monoxide. The industrial production of acetic acid is presently dominated by the methanol carbonylation process.<sup>23</sup> In this route carbon monoxide is reacted with methanol over a soluble Rh-catalyst. If such a catalyst could be made insoluble but still retaining, or rather improving the catalytic properties much would be gained from an engineering aspect at least. One way of performing this is to bind the catalyst to an insoluble support. In this work the fixation of Rh-compounds on zeolites and other metal oxides have been studied in relation to the catalytic performance in methanol carbonylation.

In selective hydrogenation of hydrocarbons the objective is to obtain a partial unsaturation. For example, benzene is easily hydrogenated to cyclohexane, which is a cheap large scale process. It would be very interesting if the hydrogenation could be stopped at the intermediate cyclohexene, because of its large potential possibilities as a raw material for the production of chemicals and polymers. Ruthenium has been shown to be a promising catalyst.<sup>24,25</sup> In this work unsupported ruthenium catalysts have been studied by ESCA to elucidate the chemistry of these catalysts. Further, the addition of compounds such as iron or titanium modifies the catalytic properties considerably. These effects have also been studied.



## Summary of Papers

### A. Vanadium Oxide Catalysts for the Selective Oxidation of Alkylpyridines.

Vanadium oxide catalysts have since long been known to undergo structural transformations during use in catalytic reactions (26). This is understandable considering the both reductive and oxidative capability, on the molecular level, of the reactant stream. Further, changes in the reaction parameters, and of the reactants, should influence the state of the catalyst, which then may be kinetically controlled. Various vanadium oxides have been detected, and the composition  $V_6O_{13}$ , in particular, is described as the selective oxidant (27,28,29). These studies have generally been based on techniques yielding information on the bulk phases.

By adding a second component a modification of the properties may be obtained and a synergetic effect with an improvement in the catalytic properties may appear.

How the reactants are interacting with the catalyst is of fundamental importance for an understanding of the catalytic chemistry. Such information may be obtained from direct adsorption measurements, but also from observations of adsorbed species present on used catalysts. In paper 1 such aspects for  $V_2O_5/TiO_2$  catalysts have been investigated. The catalysts prepared by heating the proper powder mixtures at a temperature intermediate between the melting temperatures of both oxides was found to consist of  $V^{4+}$  doped rutile particles embedded in a matrix of unstoichiometric  $V_2O_5$ . Similar results were obtained for  $V_2O_5/SiO_2$  systems. Already at an addition of about 3 mole-%  $V_2O_5$  the V/Ti atom ratio is half of that for pure  $V_2O_5$ . The catalysts surface is consequently predominantly consisting of  $V_2O_5$  and only to a smaller extent of  $TiO_2$ . It could be argued that it should be considered as a supported catalyst.

These results were mainly deduced from the quantitative ESCA analysis where calibrated sensitivity factors for  $O1s$ ,  $V2p_{3/2}$

and  $\text{Ti}2p_{3/2}$  were used. It was observed that a very thorough mixing and grinding of the oxide powder mixtures were needed to obtain a linear dependence between measured and nominal concentrations for the not fused mixtures used for calibration. This is thought to be due to a packing and shielding effect of particles of one component by particles of the other component. Inadequate mixing or different particle sizes would easily form such a situation.

Core electron binding energy (BE) shifts were determined for some oxides. There was a striking similarity of the  $01s$  line for the various oxides, which were obtained at 529,6 eV. The chemical shift in the  $\text{V}2p_{3/2}$  BE between the various vanadium oxides is rather low. A quantitative estimation of the vanadium in different oxides when present simultaneously is therefore difficult due to the overlap of the lines. However, a qualitative interpretation is quite possible. There appears to be a much greater shift in the  $\text{Ti}2p_{3/2}$  BE between different Ti-oxides.

Used catalysts were studied to reveal the steady state of the catalyst as a function of position in the bed, V/Ti ratio as prepared, and varying reaction temperatures. In used catalysts  $\text{V}_2\text{O}_5$  were found to be partially reduced, but it appeared as the rutile phase was not. The  $\text{V}2p_{3/2}$  line was asymmetrically broadened towards lower BE and this identifies a composition somewhere between  $\text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_4$ . The catalysts are only reduced in a thin surface layer, which was deduced from analysis of crushed particles. The degree of reduction is dependent on the position in the fixed bed, and increases from no reduction at the exit to the highest reduction at the inlet layers.

The temperature has a very strong influence on the state of the catalyst. The extent of reduction of the catalyst increases with the temperature up to a maximum around  $450^\circ\text{C}$  and thereafter diminishes. The catalysts seems to be easily reduced and reoxidized etc reversibly by simply changing the temperature. The temperature dependence supports the validity of the redox-mechanism in this system.

On the used catalysts there appears to be an increased amount of adsorbed species containing carbon, oxygen and nitrogen as compared with unused catalysts.

In paper 2 similar aspects for  $V_2O_5/SnO_2$  catalysts have been investigated. These catalysts are prepared by the same melting technique as the  $V_2O_5/TiO_2$  catalysts and they seem to behave similar. These also consist of two phases and the  $SnO_2$  particles are embedded in a  $V_2O_5$  matrix. The same % V (by ESCA) as for pure  $V_2O_5$  is obtained already at an addition of only about 6 mol-%  $V_2O_5$ . The catalyst surface is, as was the case for  $V_2O_5/TiO_2$ , dominated by the  $V_2O_5$  phase.

The used catalysts were studied with emphasis on activation time, molar ratio  $O_2/3$ -picoline and adsorption of pyridine-derivatives. The main activation appears to be obtained within the first approximately 30 minutes. Vanadium appears to be reduced to a state between  $V_2O_5$  and  $V_2O_4$ . The tin oxide phase seems also to be reduced to some extent. The reduction is also for these catalysts obtained in a thin surface layer. Measurements of the amounts of carbon, oxygen and nitrogen due to adsorbed species indicated an increase with the reaction time. The content of these species are approximately 7:1:1 atom ratio C:N:O according to ESCA intensities. They are thought to be due to adsorbed intermediates or products. Adsorbed pyridinecarbaldehyde at  $350^\circ C$  yield an atom ratio of 6:1:1. The mole ratio  $O_2/3$ -picoline has a great influence on the state of the catalyst and the performance. Thus, at high ratios a low degree of reduction and a high selectivity is obtained. At low ratios the catalyst is reduced considerably more. The addition of steam has the same effect as an increase in the  $O_2/3$ -picoline ratio.

Measurements on the adsorption of pyridine, pyridinecarbaldehyde, MEP and 3-picoline on the catalyst were performed by wetting the catalyst with the liquid, cooling and then running spectra at successively increased temperatures. Even at a temperature as high as  $400^\circ C$  there is still adsorbed species remaining on the catalyst. The N1s BE of these originating from MEP or 3-picoline is 399 eV, close to the value 399,3 eV for N1s observed on used catalysts. This low BE is assigned to species with no direct

involvement of the N lone pair in the interaction. Actually the formation of partially oxidized species bonded through the alkyl group is suggested.

## B. Supported Rhodium Catalysts for Methanol Carbonylation

In the carbonylation of methanol almost any Rh-compound can be used as a catalyst. The only demand is that iodide ions should be added if not present in the compound initially (30). During an initial period of the carbonylation catalytic species are formed. These are probably  $\text{Rh}(\text{CO})_2\text{I}_2^-$  - species (31,32). In the heterogenized version of the carbonylation a small amount of iodide is added continuously in the reactant feed as  $\text{CH}_3\text{I}$ , and the catalyst is a zeolite containing some Rh-species (33). These catalysts may be prepared by ion-exchange, impregnation or synthesis of a compound inside the cages of the zeolite. Little is known about the state of Rh after the preparation of the catalysts, the activation reactions and if the same active species and mechanism as for the soluble version is obtained.

In paper 3 a 0.6% Rh-zeolite ( $\text{RhCl}_3\text{NaX}$ ) catalyst prepared by reacting an aqueous  $\text{RhCl}_3$ -solution with X-zeolite was examined by in situ-treatments. The same Rh  $3d_{5/2}$  BE as for rhodium trichloride is obtained for the Rh-zeolite. Evidently, Rh is retained as Rh(III)-species in the zeolite after the preparation. The  $\text{Cl}2p$  line is very weak and corresponds to a Cl/Rh atom ratio less than 0.15. The major part of Rh is thus present in the form of Rh(III)-oxo-hydroxy-species. The Rh-content calculated by ESCA is approx. 5 times larger than the expected value, and the Rh is probably present in the outer regions of the zeolite particles to a greater extent than in the bulk.

Activation of the catalysts is performed by heating in vacuo or air at  $200^\circ\text{C}$ . The obvious effect is that water is removed from the zeolite. No effects on the structure of the Rh-species are seen up to 18 hours treatment except that there is a slight narrowing of the Rh $3d_{5/2}$  line, possibly indicating that the environment of the Rh(III)-species has become more uniform. A more severe heat treatment - a longer period of time or a higher

temperature - results in the formation of lower valence states, including the metallic state. In hydrogen reduction at 603 K a major part of the Rh-species are reduced to the metallic state. Oxygen admission results in a reoxidation, probably to  $\text{Rh}_2\text{O}_3$ . There are no great changes in the Rh/Si atom ratios upon any of the treatments, which indicates that no larger migration effects occurs.

CO adsorption on activated catalysts results in no changes in the Rh-lines but the appearance of one additional peak in the Cls spectrum. Adsorption of both CO and  $\text{CH}_3\text{I}$  results in the partial formation of lower BE rhodium species and the appearance of two additional peaks in the Cls spectrum and one  $\text{I } 3d_{5/2}$  line. A high CO/Rh and  $\text{CH}_3/\text{Rh}$  ratio and a low I/Rh ratio was obtained. It was discussed that adsorbed  $\text{I}^-$ , CO,  $\text{CH}_3^-$  and  $\text{CH}_3\text{CO}$ -species were formed. IR data suggested that  $\text{Rh(I)(CO)}_2$ -species were formed, but only about 1% of the total Rh content was involved. However, the ESCA data reveal a very high involvement of the surface rhodium, and there may be some interesting difference between external and internal rhodium in the zeolite. The ESCA data would suggest the formation of  $\text{Rh(III)-(CO)}_x$ -species in the external layer.

In paper 4 various supported Rh-catalysts were studied. Zeolites type X and mordenite were reacted with an aqueous solution of  $[\text{Rh}(\text{NH}_3)_5 \text{Cl}]\text{Cl}_2$ . The other supports,  $\text{SiO}_2$ ,  $\text{SnO}_2$  and  $\text{MgO}$  were impregnated with an aqueous solution of  $\text{RhCl}_3$ . The Rh  $3d_{5/2}$ , Nls and  $\text{Cl}2p$  core lines are, although slightly broadened, in good agreement between the pentammine rhodium salt and the  $\text{Rh}(\text{NH}_3)_5\text{Cl-X}$ . Further, the Rh:N:Cl atom ratios are close to 1:5:1, which indicates an ideal ion exchange of the  $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$  ions into the zeolite. This fact alone points to a high dispersion and bulk incorporation which also is supported by the low Rh/Si atom ratio as compared with the low dispersed surface concentrated  $\text{RhCl}_3\text{X}$  catalyst. The same result is obtained for the mordenite support.

Activation of the catalysts for carbonylation is performed by heating in nitrogen or air or vacuum. The effects on the catalyst were studied by in situ techniques. Treatment of  $\text{Rh}(\text{NH}_3)_5\text{Cl-X}$  with nitrogen or oxygen at  $400^\circ\text{C}$  led to no detectable changes



in the Rh 3d lines, but in a clear decrease in the N1s intensity. Evidently, Rh(III) is retained after loss of liganded  $\text{NH}_3$ . A more severe treatment results in production of lower valence states, and at  $600^\circ\text{C}$  heating in nitrogen a complete conversion to metallic rhodium of low dispersion occurs. Reduction in hydrogen at  $380^\circ\text{C}$  produces rhodium species with approximately 1 eV higher BE, which is interpreted as either monovalent Rh-species or zerovalent highly dispersed Rh, in which case the shift is explained by a different relaxation energy for nearly mono-dispersed Rh as compared with bulk Rh metal.

Adsorption of CO on activated zeolites lead to no detectable changes in the Rh 3d lines and indicate the formation of  $\text{Rh(III)}-(\text{CO})_x$ -species. Reaction with water saturated CO leads to a reduction of rhodium to probably Rh(I), followed by formation of  $\text{Rh(I)}-(\text{CO})_2$ -species. Treatment with both CO and  $\text{CH}_3\text{I}$  leads to no measurable effects on the Rh  $3d_{5/2}$  line, but iodine is detected, and probably adsorbed CO, I<sup>-</sup>,  $\text{CH}_3^-$  and  $\text{CH}_3\text{CO}^-$  species are formed. New features in the C1s spectra are observed for all treated catalysts, but the intensities are much lower than was the case for the  $\text{RhCl}_3\text{-X}$  catalyst. This is understandable since the Rh/Si ratio was much higher for  $\text{RhCl}_3\text{X}$ . Consequently no attempts to resolve the C1s spectra were made.

For the other catalysts -  $\text{RhCl}_3/\text{MgO}$ ,  $\text{RhCl}_3/\text{SiO}_2$  and  $\text{RhCl}_3/\text{SnO}_2$  - it was found that Rh is dominantly prevalent as Rh(III) in the first and as Rh(I) in the two latter ones. A strong interaction with the  $\text{SnO}_2$  support was suggested which can explain the lack of activity in the carbonylation reaction. The lack of activity for the  $\text{RhCl}_3/\text{SiO}_2$  catalyst is explained by the very low dispersion which was evident on the very low Rh/Si ratios found. Of the Rh(III) containing catalysts both the MgO and mordenite support catalysts show a lack of activity. The reasons are not understood for  $\text{RhCl}_3/\text{MgO}$  but for  $\text{Rh(NH}_3)_5\text{Cl-X}$  it may be caused by severe geometric restrictions. The positive effect of the type X zeolite is probably the open structure and that the Rh ions are bonded in a flexible way and easily forms coordinatively unsaturated centres.

In paper 5  $\text{Rh}_6(\text{CO})_{16}$  supported on  $\gamma\text{-Al}_2\text{O}_3$  was studied. The cluster carbonyl itself was found to have a significantly higher Rh  $3d_{5/2}$  BE than that of Rh metal although formally the valence state of Rh in the cluster is zero. This can be discussed in terms of effective atomic charge and extraatomic relaxation.

The supported cluster was after decarbonylation observed to have a higher Rh  $3d_{5/2}$  BE than the parent cluster. This indicates that oxygen is incorporated in the cluster metal framework at the loss of CO ligands. Carbonylation of these species by treatment with wet CO produces a Rh  $3d_{5/2}$  BE close to that for the parent cluster. This indicates the reversibility of the carbonylation - decarbonylation and that the cluster - support interactions are not especially strong.

A retention of the  $\text{Rh}_6$  cluster framework during low temperature treatments is discussed. Heating at  $150^\circ\text{C}$  in vacuum or in hydrogen removes the oxygen from the decarbonylated supported cluster, which is interpreted from a lowering in the Rh  $3d_{5/2}$  BE. A further decrease is obtained with evacuation or reduction at higher temperatures. However, values characteristic of Rh bulk metal were not obtained even at evacuation at  $500^\circ\text{C}$ . A conventional Rh/C catalyst, which is partially oxidized, gave bulk metal data after evacuation at  $400^\circ\text{C}$ . This difference is interpreted in terms of differences in extraatomic relaxation for very small metal particles and bulk metal.

#### C. Unsupported Ruthenium Catalysts for Liquid Phase Hydrogenation of Benzene to Cyclohexene.

Ruthenium catalysts for hydrogenation of benzene are normally prepared by precipitating a rhodium compound from an aqueous rhodium salt solution by the addition of a base solution (24) or the reverse (34), followed by pre-reduction or direct hydrogenation. Only very sparse information is available concerning the chemical state and texture of these precursors and catalysts. Further, the influence of various additions of transition metal salts on the state of the final catalyst is poorly known, although an understanding is important since these greatly improve the catalytic performance (35,25).

It is also affected by corrosion products from the reactor material of stainless steel.

In paper 6 unsupported Ru-catalysts are studied. The reaction is performed in a four phase system and this is hardly an ideal case for UHV studies. The precursor and the catalyst is obtained as a black precipitate in strong NaOH solution.

The precursor was found to consist of Ru(III,IV) hydrous oxides. In the first attempts to study the catalyst, it was thought useful not to risk a modification of the catalysts by any preparation for analysis, and therefore catalyst slurries dried in the prevacuum of the spectrometer were studied. However, upon drying the NaOH phase apparently covers the catalyst particles completely and no Ru signals are obtained. After scratching such a surface Ru 3d lines significant of Ru-metal are observed. Consequently, in the activation the precursor is reduced down to the metallic state. However, the spectra were disturbed by pump oil contamination and carbonate species formed by reaction of atmospheric carbon dioxide with sodium hydroxide. Therefore, a washing procedure was applied, and it was found that by lowering the pH to 11, the sodium hydroxide was enough diluted not to disturb the spectra.

The Ru  $3d_{5/2}$  core line with a BE of 279.9 eV and a half width of 1.9 eV obtained for the catalyst is asymmetric as usually obtained for transition metals. It is possible that a part of the asymmetry arises from additional peaks due to precursor reminiscents retained after reduction. To investigate this possibility, the catalysts were washed with hydrochloric acid to remove any hydroxides. For these samples the Rh  $3d_{5/2}$  line has a 0.1 eV lower BE and is 0.2 eV more narrow, which confirm the presence of a small portion of hydroxides. This is also inferred from the features of the O1s core line spectra.

The state of the corrosion products were studied by measuring the Fe and Cr  $2p_{3/2}$  core lines on some used catalysts. The BE of these were found to agree with that of the Fe- and Cr-hydroxides present on the stainless steel surface itself after passivation in the reaction media. The quantitative ESCA analysis give approxi-

mately the same result as the AAS data. It is suggested that the corrosion products are present as a separate phase and affects the catalytic performance mainly by surface and pore blocking.

In paper 7 the effects of iron additions on the catalyst are studied. To eliminate the influence of corrosion products the reactor material can be covered by teflon. Analysis of catalysts used in such a reactor reveals an Fe/Ru atom ratio around 0.03, which is thought to be negligible. In all catalysts ruthenium was found to be in the metallic state as in paper 6.

The iron is added in the preparational stage as an aqueous iron salt solution and very likely the incorporation in the catalyst is different than for the corrosion products. The Fe  $2p_{3/2}$  spectra reveals that iron is present in both a metallic and an oxidized state in these catalysts. Fe  $2p_{3/2}$  and  $01s$  spectra were measured on several iron oxides and iron. The oxidized iron in the catalyst can not be identified from the Fe  $2p_{3/2}$  core lines due to the very broad structure and relatively small shifts. Comparison with the  $01s$  spectra, however, suggest the presence of  $Fe_3O_4$  or  $\alpha-FeO(OH)$ . One interesting feature is obtained when plotting the atom ratio O/Ru versus the atom ratio Fe/Ru. Namely, that extrapolation to zero yield an O/Ru ratio of approximately 0.7 for the iron free catalyst. This is the same order of magnitude as could be expected from a monolayer of hydroxide.

To investigate if the metallic iron present in this system was alloyed with ruthenium, the catalysts were washed with concentrated HCl to remove the iron oxides and any iron phase. After such treatment an almost pure metallic Fe  $2p_{3/2}$  line is obtained. Further, it is stable towards oxidation and it is concluded that an Fe-Ru alloy is present. It is suggested that in the preparational stage of the precursor preparation, there is a formation of both Fe-Ru mixed hydrous oxides and iron hydrous oxides. During activation the mixed hydrous oxide is reduced down to the alloy form whereas the iron hydrous oxide remains intact.

Preparation from two different solutions of iron(II) sulphate results in catalysts for which the correlation between the atom ratio Fe/Ru by ESCA and the nominal Fe/Ru atom ratio yield two

different lines. After subtracting an iron amount proportional to corrosion products a good correlation with the nominal ratios is obtained for the stock solution prepared series. The series prepared from fresh solutions, however, yield considerably lower Fe/Ru ratios than expected. The effects are interpreted as arising from differences in particle size between the iron hydroxides in the two series. Interesting results are obtained when plotting the rate of hydrogenation of benzene and the maximum yield of cyclohexene versus the Fe/Ru atom ratios obtained by ESCA. Then data for both series fall on the same curves, which is not obtained if using nominal ratios. This is explained by the fact that the series with larger particles of iron hydroxides would need a larger nominal addition of iron to obtain the same coverage on the Fe-Ru surface. The hydrogenation rate decreases with increased iron additions and the yield of cyclohexene shows a maximum at an Fe/Ru ratio of 0.16. It is very suggestive that this ratio corresponds to a blocking of every 6th Ru atom on the average, which would yield an inhibition of the planar adsorption of benzene.

In paper 8 the effects of titanium additions are studied. The addition is made at the preparation of the precursor. Only used activated catalysts are studied.

The quantitative analysis reveal a reasonable correspondence between the Ti/Ru atom ratios by ESCA and the nominal ratios underlining the relatively homogeneous nature of the catalysts. The Ti  $2p_{3/2}$  BE indicates the presence of Ti in the +4 valence state for all compositions of Ti/Ru although it is slightly lower than for  $TiO_2$ . The O1s spectra show great variations with changes in the Ti/Ru ratio. The spectra can be resolved in three components representing physisorbed water, hydroxide groups and lattice oxygen. The intensity of the latter increases with the Ti/Ru ratio and corresponds well with the value for  $TiO_2$ .

The Ru  $3d_{5/2}$  core line appears to shift continuously from 279.9 eV for metallic Ru with no Ti addition up to 281.6 eV, similar to the Ru(III,IV) hydrous oxide, at the highest Ti-addition. A closer inspection of the Ru 3d BE region reveal that spectra from all catalysts can be resolved in components representing two different ruthenium species, - the hydrous oxide and the metal - and



carbon contamination. The interesting feature is that the ratio of ruthenium metal to ruthenium hydroxide is decreasing with increased titanium additions. This fact, the presence of the oxidized Ru and the low value of the  $Ti\ 2\ p_{3/2}$ , leads to the conclusion that a mixed Ru-Ti hydrous oxide formed in the precipitation of the precursor is not reduced in the activation procedure. Ru hydrous oxide present in a separate phase is reduced, however, which explains the formation of Ru-metal.

The rate of hydrogenation decreases with increased titanium additions, which is caused by the reduced amount of ruthenium in the metallic state. After correction for the influence of corrosion a linear correlation is obtained.

#### Acknowledgements

I wish to express my appreciation to Professor Sten T. Lundin for his encouragement, generous support and interest during this work.

Appreciation is also extended to Dr. Sven Järås, Dr. Michael S. Scurrrell, Prof. Russell F. Howe and Civ.ing. C. U. Ingemar Odenbrand for their inspiring collaboration and helpful discussions.

Special gratitude is expressed to Civ.ing. Arne S. Andersson and Dr. Lars-Erik Johansson for inspiring discussions.

I also want to thank Dr. Gunnar Schön who introduced me into the field of photoelectron spectroscopy and Dr. Ragnar Larsson for frequent extensions of the ESCA facilities.

Gratitude is also expressed to Mr. Lars Engström and to Mr. Samuel Kiuru for valuable assistance and to Mrs Gunilla Cederholm and Mrs Ingegerd Bengtsson for typing some manuscripts.

Finally, I wish to thank my family for their encouragement and patience.

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HYDROGENATION OF BENZENE TO CYCLOHEXENE ON AN  
UNSUPPORTED RUTHENIUM CATALYST: An ESCA Study of  
titanium poisoned catalysts.

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## SYNOPSIS

ESCA data show that the addition of titanium to a ruthenium catalyst gives a catalyst containing some metallic ruthenium and a mixed titanium-ruthenium hydrous oxide. The ratio of ruthenium in the metallic form to ruthenium in the hydrous oxide form decreases with increasing titanium concentration. The poisoning effect of the titanium addition on the hydrogenation activity results from the reduced amount of ruthenium metal available.

## 1. Introduction

An increased interest in ruthenium as a catalyst for the selective hydrogenation of benzene to cyclohexene has recently been shown<sup>1-6</sup>. To further our understanding of how the catalyst works we recently made an investigation on the texture and chemistry of pure Ru-catalysts<sup>7</sup>. It has been shown that poisoning of the catalyst by addition of iron and titanium compounds influences both the yield of cyclohexene and the reaction rate<sup>1</sup>. The effects of the iron additions on the texture and chemistry of the catalyst were recently characterized by physical and chemical techniques<sup>8</sup> and we have now extended these studies to an investigation of the titanium poisoned catalysts by X-ray photoelectron spectroscopy.

## 2. Experimental

### 2.1 Preparation

The materials used were ruthenium(III)chloride hydrate (Fluka AG, purum, 10-15% water), titanium(III)chloride solution (BDH Technical, 15% w/v  $\text{TiCl}_3$ ), sodium hydroxide (EKA, 98.6%), and  $\text{TiO}_2$  (Riedel-De-Haen AG, purum).

The catalysts were prepared by adding appropriate amounts of titanium(III)chloride to a stock solution of ruthenium(III) chloride in distilled water from which solids were precipitated in a Parr pressure reactor<sup>2</sup> following instantaneous addition of 9.6 M sodium hydroxide to a final

concentration of 1.19 M. After the hydrogenation experiments, the catalyst slurry was washed with several portions of 0.01 M NaOH, decanted and dried by evacuation at room temperature before ESCA analysis.

## 2.2 ESCA studies

The procedure for the ESCA measurements have been described elsewhere<sup>7</sup>. They were performed on an AEI ES200B electron spectrometer, equipped with an Al-anode (1486.6 eV). The full width at half maximum (FWHM) of the Au 4f<sub>7/2</sub> line was 1.8 eV. Sample charging was corrected for with the Au 4f<sub>7/2</sub> line at 83.8 eV. In the quantitative ESCA analysis - as described elsewhere<sup>2</sup> - the sensitivity factors were C 1s = 1, O 1s = 2.7, Ru 3d<sub>5/2</sub> = 7.4 and Ti 2p<sub>3/2</sub> = 4.8. Some spectra were digitized and smoothed<sup>9</sup> on a Tektronix 4051 with a 4662 interactive digital plotter. A quadratic smoothing over a number of points taken as 0.7x(FWHM) was used<sup>10</sup>. End points which normally are lost were estimated with a linear least squares fit<sup>10</sup>. Some peak envelopes were simulated by adjusting the position and width of the selected Gaussian components until a correct fit in the least squares approximation of the magnitudes was obtained. The base line for the O 1s peak was approximated to a straight line. The Ru 3d peak showed a much higher slope in the base line and it was necessary to make allowance for this effect - arising from inelastic scattering - in the calculations<sup>11</sup>.



### 3. Results and discussion

Catalysts prepared by precipitation of  $\text{RuCl}_3$  and  $\text{TiCl}_3$  aqueous solutions show great changes in activities and selectivities with the Ti/Ru ratio<sup>2</sup>. Some catalysts used in the hydrogenation have been examined by ESCA to gain information on the chemical state of Ru and Ti. The atom ratio Ti/Ru as revealed by ESCA is shown in Figure 1 as a function of the bulk atom ratio Ti/Ru. With the sensitivity factors used there is a deviation of less than 10% from the theoretical Ti/Ru line. The fact that the Ti/Ru atom ratio by ESCA does not deviate much from the Ti/Ru atom ratio as prepared - and has a linear correlation - shows that Ti and Ru are present either in one phase with no surface segregation effects<sup>12</sup>, or in two separate phases with comparable particle sizes<sup>13</sup>.

The binding energies for Ru  $3d_{5/2}$ , Ti  $2p_{3/2}$  and O  $1s$  are given in Table 1. The Ti  $2p_{3/2}$  core line has a fairly constant value around 457.6 - 457.8 eV for the four catalysts with various Ti/Ru ratios, indicating the similarity of the Ti - compounds in these different catalysts. The O  $1s$  line, however, changes very much as seen in Figure 2. Spectrum C, obtained with the catalyst with the highest titanium loading, clearly shows that there is one major oxygen component at 529.6 eV, which is the value obtained for lattice oxygen in  $\text{TiO}_2$ . The component at 531.1 eV is assigned to hydroxide oxygen and the one at 532.7 eV to physisorbed water. The spectra A and B

in Figure 2, for the catalysts with Ti/Ru ratios of 0.23 and 0.58, show a much broader structure indicating a larger amount of the higher B.E. oxygen species. The structure is complicated by the fact that the samples with higher ruthenium content probably contain significant amounts of other oxygen-containing species in combination with ruthenium. However, it is clear that the amounts of the low and perhaps middle B.E. components are increasing with increasing titanium content. This would suggest the presence of  $\text{TiO}_2$  or rather hydrated  $\text{TiO}_2$ . It is known from Pourbaix diagrams<sup>14</sup> that  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  and  $\text{TiO}_2$  are the stable species under the hydrogenation conditions used. Further, hydrated  $\text{TiO}_2$  upon ageing forms  $\text{TiO}_2$  and water, even in aqueous media<sup>15</sup>. However, the Ti  $2p_{3/2}$  B.E. are slightly lower than for  $\text{TiO}_2$  (see Table 1). Considering that titanates have a Ti  $2p_{3/2}$  B.E. lower by 0.4-0.7 eV than that found with  $\text{TiO}_2$ <sup>16</sup>, we suggest that a ruthenium titanate has formed in our samples. It is probably an ill-defined precipitate and should perhaps rather be called a mixed ruthenium - titanium hydrous oxide.

Considering the Ru  $3d_{5/2}$  core line B.E., it is seen in Table 1 that apparently a continuous shift occurs from 279.9 up to 281.6 eV with the addition of titanium. The Ru 3d spectra are shown in Figure 3. It is evident that the Ru  $3d_{5/2}$  line with an increased Ti/Ru ratio is broadened and shifted towards higher B.E. The spectra

are disturbed by the presence of the C 1s core line from carbon contaminations. The estimated C/Ru atom ratio increases with titanium addition from 0.2 up to 0.9 for the sample with the highest Ti/Ru ratio. However, this change is caused by the decreasing Ru-content since the C/(Ti+Ru) atom ratio remains fairly constant at around 0.2. The apparent continuous shift in the Ru  $3d_{5/2}$  B.E. can be explained by the presence of two different ruthenium species with a change in their relative amounts for the four catalysts. The spectra in Figure 3 have been resolved into four Gaussian components representing Ru  $3d_{3/2}$  and  $3d_{5/2}$  for ruthenium hydroxide and for ruthenium metal and in addition two Gaussian components representing the C 1s line for carbon contamination. All components are added to the base line as described above. The C 1s lines are placed where usually observed, that is around 285 eV with a shoulder towards higher B.E. The interesting feature seen in the resolved spectra is that the ratio of ruthenium metal to ruthenium hydroxide is changing with titanium content. (See also  $Ru^O/Ru^{total}$  in Table 1). The ruthenium metal 3d line should be asymmetric due to the excitation of hole-electron pairs<sup>17</sup>, which is not expected for the ruthenium hydroxide. An estimation of this effect is given in table 1 where  $Ru^O/Ru^{total}$  ratios corrected for the asymmetric line shape are included. This was done by assuming that the same ratio of the two low B.E. Gaussian curves in the pure Ru-catalyst is re-

presentative of the asymmetric metal line shape for all samples. The result is only to give slightly higher ratios but the overall trend remains.

The addition of titanium prevents the reduction of all of the ruthenium and this indicates the presence of some mixed hydrous oxides. The preparation of the catalyst is performed with aqueous  $\text{RuCl}_3$  and  $\text{TiCl}_3$  which probably contain ions of the valence states +3 and +4. Since the solubility products<sup>15,18</sup> are  $\approx 10^{-38}$  for  $\text{Ru}(\text{OH})_3$ ,  $\approx 10^{-44}$  for  $\text{Ru}(\text{OH})_4$  and  $\approx 10^{-54}$  for  $\text{Ti}(\text{OH})_4$  it seems likely that the initial precipitate partly consists of a mixed  $\text{Ru}(\text{III,IV}) - \text{Ti}(\text{III,IV})$  hydrous oxide in addition to the individual hydroxides. Titanium(III)-hydroxide is easily converted to  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  by the oxygen present in the solution<sup>15</sup>. Since the titanium dioxide is not reduced under the present hydrogenation conditions it seems likely that the coprecipitated ruthenium hydroxide is not reduced either. However, any ruthenium hydroxide present as a separate phase would be reduced. From Table 1 one may deduce a Ti/Ru ratio for the mixed hydrous oxide which is close to one for the two catalysts with lower titanium additions. The mixed hydroxide could perhaps be regarded as a ruthenium titanate hydrate by analogy with co-precipitated Mg and Ti-hydroxides<sup>19</sup>. However, for those samples containing a surplus of titanium the Ti/Ru ratios for the mixed hydroxide is approximately 1.7 and 4 respectively, and it is then necessary that

the excess of titanium is present in a separate hydroxide phase.

In Figure 4 the dependence of the rate of hydrogenation on the amount of ruthenium metal taken as  $\text{Ru}^{\text{O}}/\text{Ru}^{\text{total}}$  is shown. Since all batches contain the same amount of ruthenium and since the ESCA analysis reveals the surface content this ratio should be proportional to the amount of ruthenium metal available for catalytic hydrogenation. There is apparently a linear dependence of the hydrogenation rate on the amount of ruthenium metal. The fact that the line does not go through the origin can be explained by poisoning effects, caused by metallic species corroded from the reactor walls during the hydrogenation experiment.

In order to clarify this question the rate of dissolution of iron was measured at 366 K and recalculated to the hydrogenation temperature (389 K) as before<sup>1</sup>. The rate of hydrogenation was then corrected for the poisonous effect of iron and these values are also shown in Figure 4 (dashed line). It is clear that this correction gives a much better correlation indicating that the rate of hydrogenation is proportional to the unpoisoned metallic Ru surface area.

#### Acknowledgements

Both authors are grateful to Prof. S-T. Lundin for his generous support.

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Table 1. Binding energies and half widths<sup>a</sup> (eV) of Ru 3d<sub>5/2</sub>, Ti 2p<sub>3/2</sub> and 0 1s core lines and atom ratios of Ti/Ru and Ru<sup>O</sup>/Ru<sup>total</sup> for some titanium-ruthenium catalysts.

| <u>Sample</u>                      | <u>Ru 3d<sub>5/2</sub></u> | <u>Ti 2p<sub>3/2</sub></u> | <u>0 1s<sup>b</sup></u> | <u>Ti/Ru</u> | <u>Ru<sup>O</sup>/Ru<sup>total</sup></u> |
|------------------------------------|----------------------------|----------------------------|-------------------------|--------------|------------------------------------------|
| Ru-catalyst precursor              | 281.5<br>(2.5)             |                            | 531.1-529.4             |              |                                          |
| Ru-catalyst                        | 279.9<br>(1.9)             |                            |                         |              | 0.84 (1) <sup>d</sup>                    |
| Ti/Ru catalyst (0.23) <sup>c</sup> | 280.1<br>(2.5)             | 457.8<br>(2.8)             | 531.2<br>(5.7)          | 0.20         | 0.61 (0.73) <sup>d</sup>                 |
| Ti/Ru catalyst (0.58) <sup>c</sup> | 280.4<br>(2.8)             | 457.7<br>(2.5)             | 531.0<br>(4.9)          | 0.44         | 0.52 (0.62) <sup>d</sup>                 |
| Ti/Ru catalyst (1.15) <sup>c</sup> | 281.3<br>(3.4)             | 457.7<br>(2.1)             | 530.9<br>(4.7)          | 1.25         | 0.21 (0.25) <sup>d</sup>                 |
| Ti/Ru catalyst (2.81) <sup>c</sup> | 281.6<br>(3.4)             | 457.6<br>(2.2)             | 530.2<br>(3.4)          | 3.17         | 0.18 (0.21) <sup>d</sup>                 |
| TiO <sub>2</sub>                   |                            | 458.5<br>(1.7)             | 529.6<br>(2.0)          |              |                                          |

a FWHM within parenthesis

b Taken at half height

c Ti/Ru atom ratio as prepared

d Corrected for asymmetric line shape of the metal Ru 3d lines.

Figure 1

Atom ratio Ti/Ru obtained by ESCA analysis versus the atom ratio Ti/Ru as prepared.

Figure 2

O 1s electron spectra from some Ti-Ru catalysts with various Ti/Ru atom ratios (as prepared). A. 0.23, B. 0.58, C. 2.81 and D.  $\text{TiO}_2$ . Spectrum C is resolved in three Gaussian components.

Figure 3

Ru 3d binding energy region electron spectra from some Ti-Ru catalysts with various Ti/Ru atom ratios.

A. 0, B. 0.23, C. 0.58, D. 1.15, E. 2.81

The spectra are resolved in two sets of two Gaussian curves ( $\text{Ru } 3d_{3/2}$  and  $\text{Ru } 3d_{5/2}$ ) representing ruthenium metal and ruthenium hydroxide respectively (Dashed lines). C 1s lines from carbon contaminations are presented by two Gaussian curves (Solid lines).

Figure 4

Rate of hydrogenation (from ref 2) versus atom ratio  $\text{Ru}^{\text{O}}/\text{Ru}^{\text{total}}$  by ESCA for titanium poisoned catalysts.

○ measured by ESCA, □ corrected for the influence of corrosion products.

Figure 1

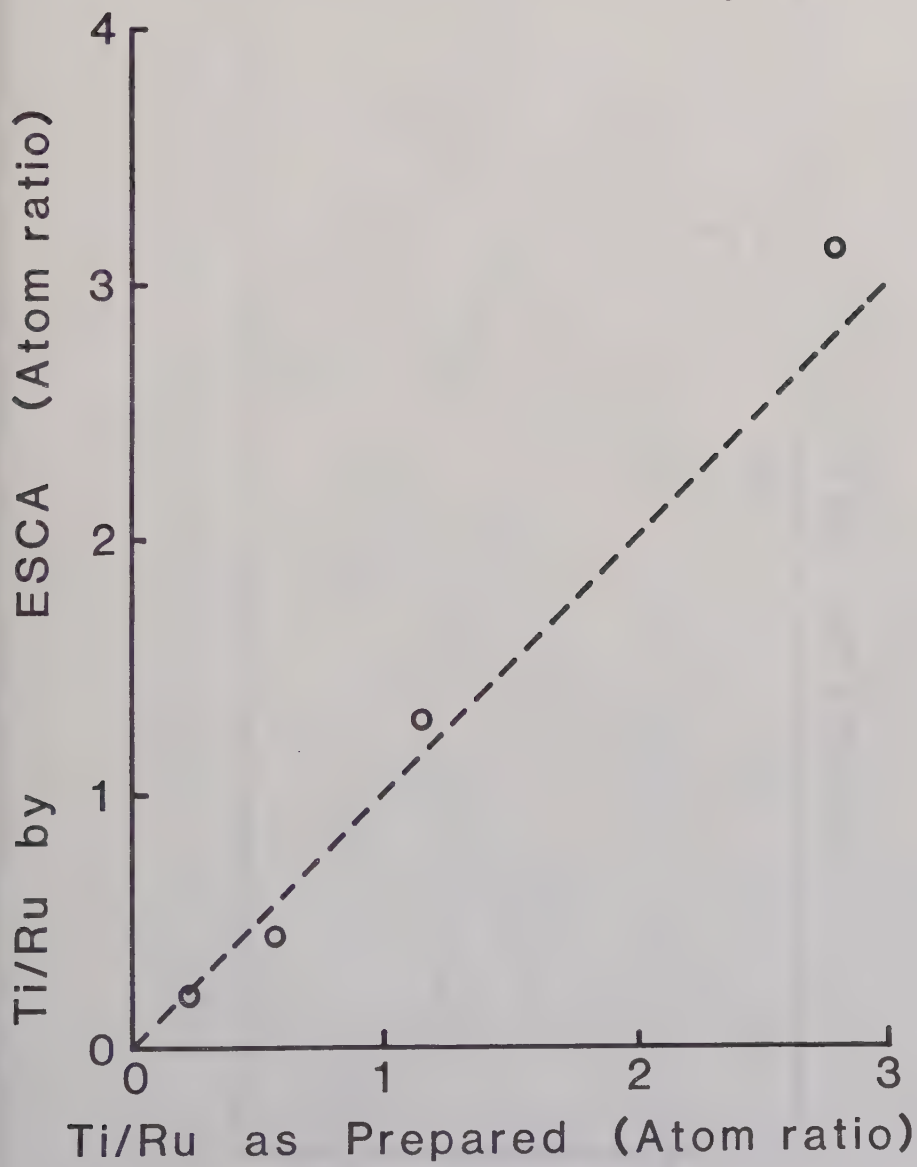


Figure 2

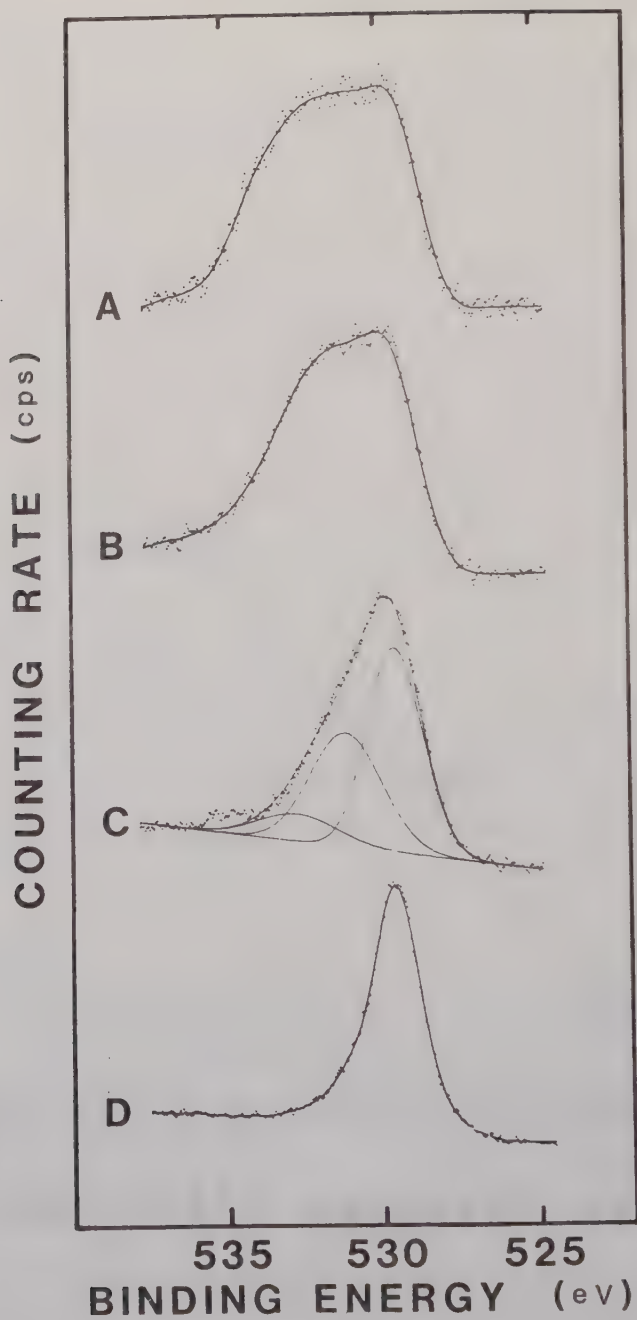


Figure 3

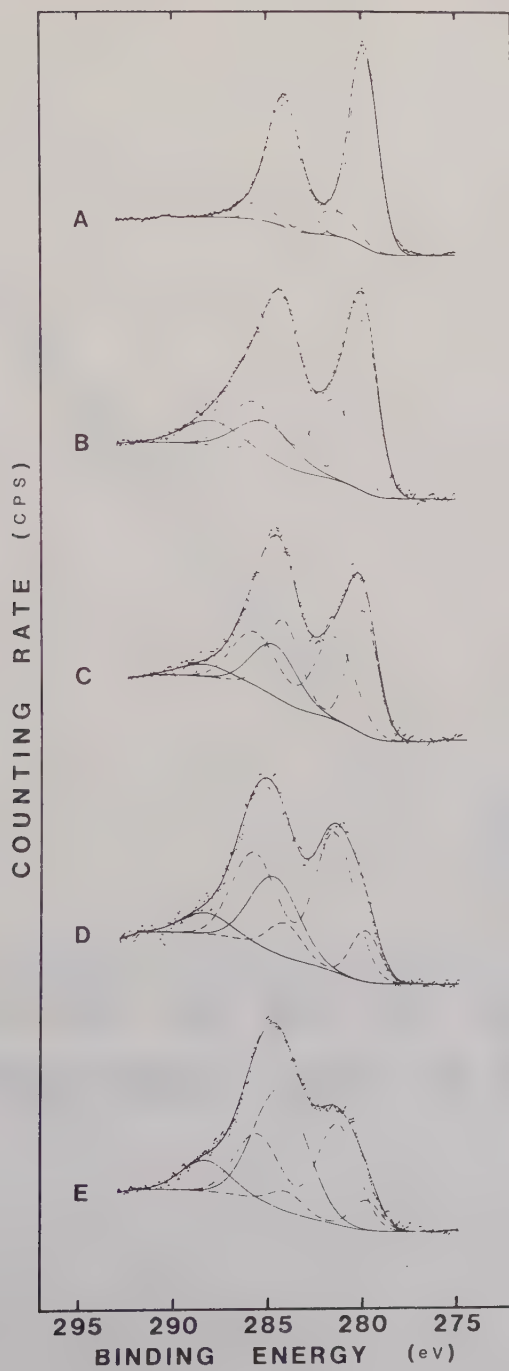




Figure 4

